

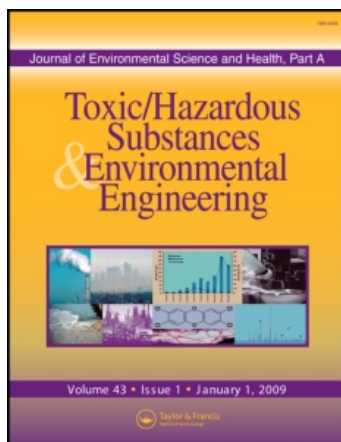
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Characterization of Odors from Limed Biosolids Treated with Nitrate and Anthraquinone

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Complaints from the public due to odor emissions are one of the biggest problems associated with any biosolids land application program. Chemical additives to reduce or mask odors are one option for producers; however, many chemicals are too expensive or are too unstable to use safely. This project provides a preliminary evaluation of nitrate or nitrate + anthraquinone as additives in controlling odors from limed biosolids. Over a twenty-four day period, odors were measured in the headspace over several treatment levels using two different chemical analysis tools along with olfactometric evaluation of odor intensity and hedonic tone. On six days during the sample period, hydrogen sulfide was measured using a Jerome 631X, a sensor that also responds to other reduce sulfur gases. Other specific sulfides, amines, and mercaptans were also determined using solid phase microextraction with gas chromatography-mass spectrometry. A simple sniff test approach was used with six panelists on five days during the project. The chemical analysis results revealed that the addition of nitrate and especially nitrate + anthraquinone was effective in reducing concentrations of hydrogen sulfide and methylmercaptan when compared to untreated limed biosolids. However, the olfactometric results did not reveal any significant differences between treatments. The panelists also found that all treatments exhibited a fishy or ammoniacal character, indicative of amines, or ammonia. More advance olfactometric analysis utilizing dilution techniques might have been able to distinguish between treatments, but it is likely that amines were the dominant odorant released from all treatments. This preliminary project suggests that chemical addition of nitrate or nitrate + anthraquinone would be most effective in controlling odors from unlimed biosolids such as anaerobically digested materials.

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Key Words: Anthraquinone; Biosolids; Nitrate; Odor panel; Sulfur compounds; Trimethylamine.

INTRODUCTION

Offensive odor is a significant problem for the land application program at many wastewater treatment facilities. Although most unit processes in a wastewater treatment plant are potential sources of odor, solid-handling systems, such as thickening, drying, and lime stabilization are normally the most significant.^[1] The final biosolids product, which can be used as a soil amendment, often also emits offensive odor, causing public resistance to large scale land application programs and results in increased regulatory action.

Chemical treatments, especially oxidation technologies, have been applied to control odors from wastewater and sludge since the 1970s.^[2] Hydrogen peroxide has been applied to oxidize H₂S, mercaptanes, thiosulfate, and sulfur dioxide in wastewater,^[2] and waste activate sludge.^[3] However, hydrogen peroxide can be dangerous to handle and takes time to react,^[4] so several other oxidants also have been tested and applied. For example, potassium permanganate was added to raw dewatered sludge to reduce hydrogen sulfide production.^[4] Farooq and Akhlague^[5] tested ozone to condition and oxidize heavy metals and organics in raw and thickened waste activate sludge. They reported a considerable reduction in odor released from the sludge, although they did not quantify their results. De Luca et al.^[6] used potassium ferrate to stabilize dewatered sludge and compared its performance with lime stabilization in terms of odor control. They found that ferrate was very effective in oxidizing reduced sulfur and nitrogen compounds and mitigating odors from conditioned sludge. Gao et al.^[7] used sodium hypochlorite to remove 95% of hydrogen sulfide from gas emissions released from gravity thickened sludge.

While results of these studies are encouraging, none of the oxidants are widely used, mainly due to high costs. Odor control through the use of hydrogen peroxide, permanganate or hypochlorite, requires large quantities of chemicals for conditioning or oxidizing reduced compounds in sludge. For example, to treat 1 mol of sulfide in sludge 2–5 mol of hydrogen peroxide are required.^[3] Although relatively small amount of ozone and potassium ferrate is required to oxidize odorants in sludge, they are expensive to produce and they require special handling.

Lime stabilization is used to condition dewatered sludge and is added to final biosolids in approximately 20% of wastewater treatment plants in the US due to its economical advantage over other chemical stabilization technologies.^[8] Lime is added to raw sludge until the pH is > 12. The high pH environment and exothermic reaction inactivates microorganisms in sludge and produces a soil like final product. In addition to its disinfection abilities, lime

addition is believed to reduce odors in sludge. However, there are still complaints about odors from limed biosolids on site and in the field where it is land-applied. Odors from limed biosolids, are often characterized as “fishy” and “decaying,” pose a major obstacle to the land application program. The fishy and decaying odors are characteristics of amines (especially trimethylamine: TMA) and reduced sulfur compounds (produced under septic conditions), respectively.^[9]

Recently, it was demonstrated that H₂S in sewer systems and wastewater under reducing condition could be diminished by adding nitrate.^[10–12] They also reported anthraquinone added with nitrate enhanced H₂S control. The theoretical basis for the addition of nitrate is that the oxidation state of the system is changed such that nitrate rather than sulfate is reduced. The addition of anthraquinone inhibits the long term growth of odor causing microbes.

In this preliminary study, effects of nitrate and anthraquinone addition to limed biosolids were evaluated with respect to odor quality. This study was initiated with the assumption that if these oxidants block the formation of reduced sulfurs, the odor quality of the final product will be improved. The evaluation of odors from biosolids with and without treatment using the chemicals was carried out using a simple odor evaluation approach along with a gas analytical method utilizing solid phase microextraction coupled to gas chromatography-mass spectrometry. The specific goals of the current study were as follows:

- (i) Evaluation of intensity and hedonic tones of odors from limed biosolids with and without nitrate and anthraquinone treatment over 20 days.
- (ii) Characterization and quantification of specific odorants in the headspace over limed biosolids with and without nitrate and anthraquinone treatment.
- (iii) Preliminary assessment of the effectiveness of these chemicals in controlling odors in limed biosolids and provision of recommendations for further.

MATERIALS AND METHODS

Sample Preparation

Two different chemical additives, i.e., Bioxide© and Bioxide©-AQ that are commercially available were obtained from USFilter, Inc. (Warrendale, PA). The first mainly consists of Ca(NO₃)₂ (425 g NO₃⁻/L Bioxide). The second additive was made by adding 12.2 g of anthraquinone to 1 L of Bioxide.

Unlimed dewatered sludge (25% solids, a blend of gravity thickened sludge and waste activated sludge), collected from a centrifuge in the Blue Plains Wastewater Treatment Plant located in Washington, DC, was mixed with lime and Bioxide in a pilot scale industrial mixer at Blue Plains. Lime was added

Table 1: Sample matrix under study.

Sample ID	Control	BL	BM	BL-AQ ^a	BM-AQ ^a
Dosage of Bioxide ^b	0	0.1	0.5	0.1	0.5

^aContains anthraquinone of 100 lbs/1000 gallons of Bioxide.

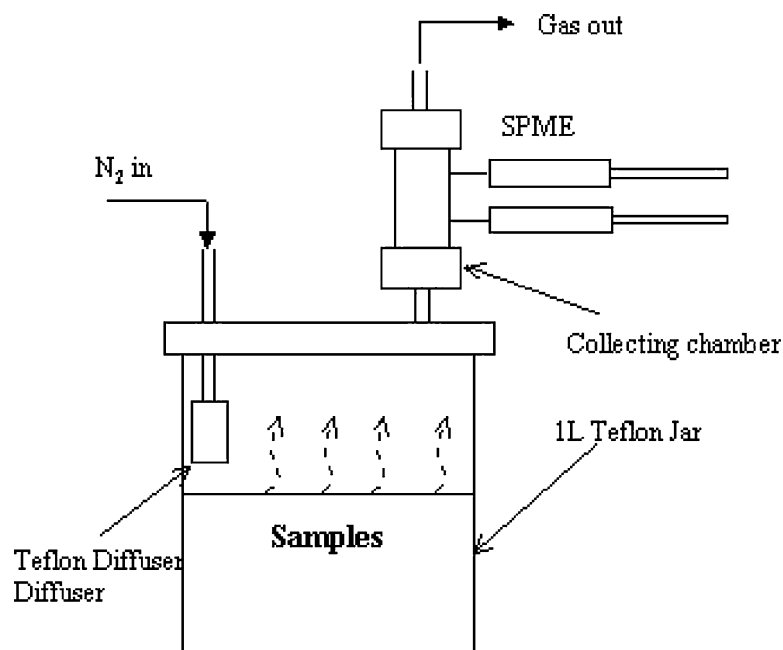
^bUnit of dosage: gallon/ton of dewatered sludge (wet basis).

to the sludge sample at 25% by mass. In each batch, biosolids of 1 wet ton was mixed with lime and the additives in the mixer. Table 1 presents the treatments that were used to assess the effect of both Bioxide and Bioxide-AQ.

Analysis of Odorants

Triplicate aliquots of each of the five treatments were collected from the mixer and transferred to 1-L Teflon containers, and transported to the nearby U.S. Department Agriculture Agricultural Research Service Environmental Quality Laboratory located in Beltsville, MD. Upon arrival, the samples were stored sealed in a hood at 25°C. In order to monitor the dynamic change of odorants from biosolids, they were measured at six different times for the study period; 1, 5, 10, 15, 20, and 24 days after the treatment.

The headspace of each Teflon jar was analyzed for specific odorants using a flow through system to expose solid phase microextraction (SPME) fibers (Fig. 1). Just prior to extraction, the headspace of each sample jar was flushed

**Figure 1:** Experimental set-up for instrumental analysis.

with pure nitrogen gas at a constant rate of 72 mL/min. A 75 μ m SPME fiber coated with Carboxen-Polydimethylsiloxane (Car-PDMS) was exposed to the flowing gas as a means to capture trimethylamine (TMA), carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methyl mercaptan (MSH), ethyl mercaptan (ESH), propionic mercaptan (PSH), and butyl mercaptan (BSH) (Supelco, Bellefonte, Pennsylvania, USA). Car-PDMS has been successfully used for the analysis of TMA and reduced sulfurs in the headspace of thickened sludge,^[1] limed biosolids,^[9] heat-dried pellets,^[13] and commercially available composts.^[14] The exposure period for the SPME fibers to the gas was 1 h. After the extraction, fibers were directly injected into a GC/MS system (Hewlett Packard 5890 gas chromatograph coupled to HP 5988 mass spectrometer) for quantification. The details of the GC analysis, calibration of SPME, GC temperature program etc., can be found elsewhere.^[15]

Sample off-gas was also evaluated for total reduced sulfur (TRS) using a Jerome 631X Hydrogen Sulfide Analyzer (Arizona Instrument, Phoenix, AZ) in parallel with SPME analysis. The Jerome 631X is most sensitive to H_2S but also reacts to other reduced sulfur gases and has a limit of detection (LOD) of 0.003 ppm.^[16]

Odor Evaluation

Another set of aliquots from each treatment were transferred into 2-gallon buckets, which were stored in a laboratory of the Blue Plains WWTP at room temperature for evaluation by a 6 member odor panel. A quarter inch hole was made in the lid of each bucket. The evaluation panel was not involved in preparation of the samples and did not know which samples were treated. Each panel member was asked to sniff the odors through the hole in the lid and score the odor intensity and hedonic tone of each sample. Odor intensity and hedonic tone were arbitrarily scaled 0 (weakest) \sim 10 (strongest) and -10 (worst) \sim 0 (not bad), respectively. They were also asked to briefly describe the character of the odor. Panel testing was conducted six times during the testing period (i.e., 4, 5, 10, 15, 19, and 24 days after the treatment). Therefore, chemical analysis coincided with odor panel evaluations only on days 5, 15, and 24.

RESULTS AND DISCUSSION

Analysis of Odorants with SPME Coupled with GC-MS

Analysis of specific odorants over time clearly revealed the benefits of the Bioxide treatments. Bioxide was effective in reducing the production of sulfur compounds from the biosolids. The addition of the Bioxide, especially Bioxide-AQ, was effective in the reduction of total reduced sulfurs (Fig. 2(b)). In the beginning, the level of TRS from the control could not be evaluated since it was

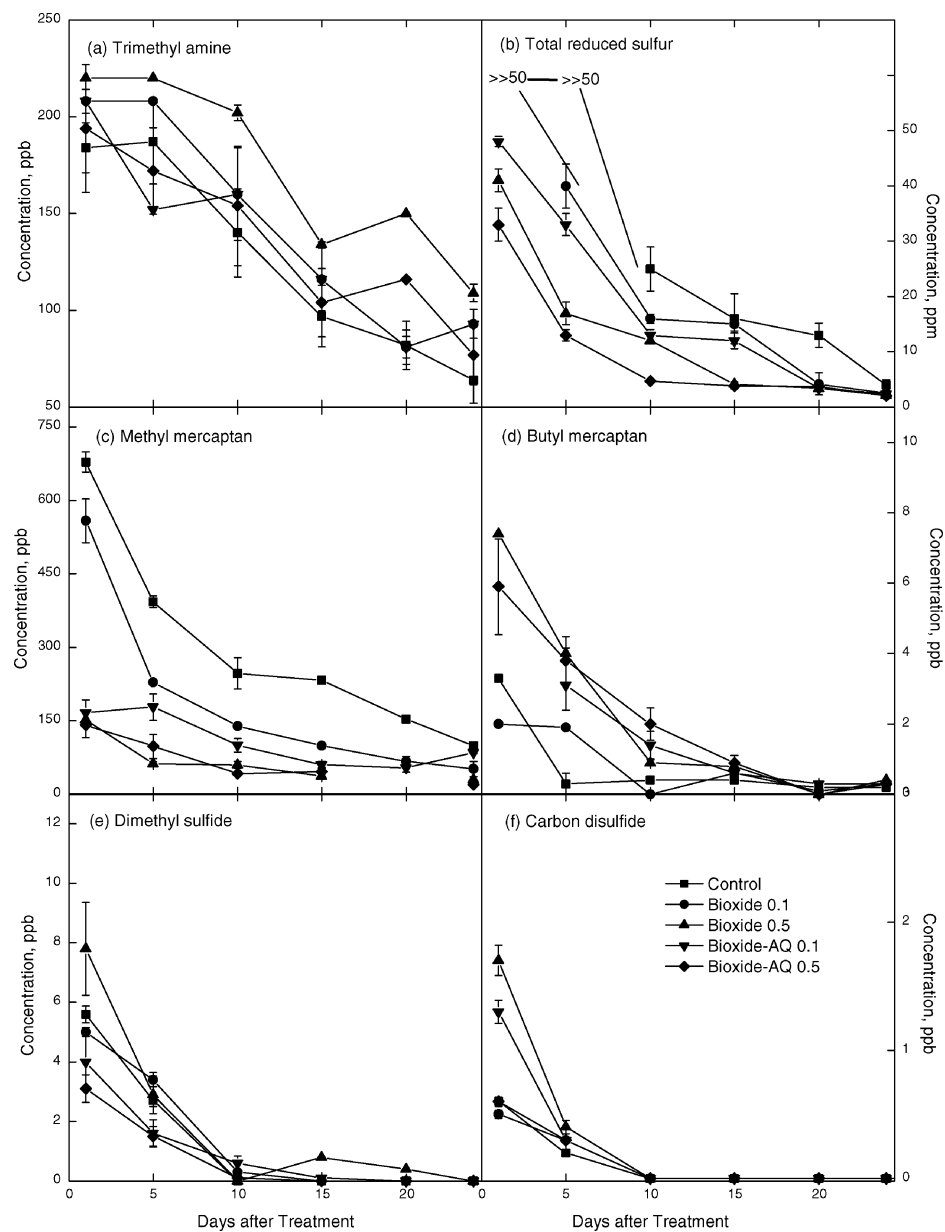


Figure 2: Time profiles of odorants analyzed using GC-MS (error bars represent standard deviation of three replicates).

over the limit of instrument's maximum detection level (50 ppm). However, TRS produced from the sample with Bioxide-AQ of 0.5 gal/ton of wet biosolids was less than 50% of the control. The Jerome 631X may be tracking MSH levels in the headspace since the trend is quite similar to the TRS (Fig. 2(c)). One

day after the treatment, the control produced about 700 ppb of MSH, while the samples with the additives produced approximately 150 ppb except the Bioxide 0.1 gal/ton of wet biosolids treatment, which produced about 550 ppb.

As for BSH, DMS, and CS₂, the concentration of these compounds in the headspace of all samples was lower than 10 ppb with no clear trend in results. Considering their odor thresholds, 1 ppb, 0.1 ppb, and 16 ppb for BSH,^[17] DMS,^[18] and CS₂,^[19] respectively, the contribution to the overall odors from those compounds is likely minimal (especially 5 days after the treatment). ESH and PSH were not detected in any samples. However, DMDS, which is believed to be one of major odorants from limed biosolids,^[9] could not be compared in this study, since the concentration levels exceeded the quantification range of the current method ($\gg 100$ ppb) for all treatments on all days.

Therefore, MSH (odor threshold of 2.1 ppb^[20]) and DMDS (odor threshold of 6.4 ppb^[21]) were the major sulfur compounds among the eight included in the method. H₂S was likely present but with our current instrument H₂S could not be quantified independently. Even though further experiments are needed to evaluate the effects of Bioxide on DMDS, based on the time profiles of TRS and MSH, it appears that Bioxide is effective in reducing the production of some key sulfur compounds.

As for TMA (odor threshold of 0.21 ppb^[22]), similar levels were produced from all the samples (Fig. 2(a)). Results were not distinguishable between treatments and fell between 175–225 ppb on Day 1 and dropped to 75–125 ppb on Day 24, although the Bioxide of 0.5 gal/ton treatment was slightly higher than others. This result is logical, since Bioxide is mainly made of Ca(NO₃)₂ and should not affect the TMA concentration. The TMA was persistent over the period of study, as seen in the previous study characterizing odors from limed biosolids.^[9]

Odor Evaluation

Results from the odor evaluation panelists showed a high level of variability over the entire study period but with a general trend of high initial odor followed by a relatively constant level for all treatments (Fig. 3(a)). Odor intensity and hedonic tone values varied greatly between panelists, which is not uncommon in odor panel testing, especially when samples are not delivered in a controlled manner to the nose.^[23] Under these conditions, it was not possible to distinguish treated samples from the control. All treatments showed similar levels of odor intensity for each testing day. Over the entire period of study, a reduction in odor intensity could be only detected between the first and second odor panel testing performed on Day 4 and Day 5 after the treatment, respectively. However, the difference cannot be verified, since the first odor panel study was performed by lifting the lid of each sample bucket. The samples had been stored in closed buckets for 4 days before the test. Therefore, the odorants might have

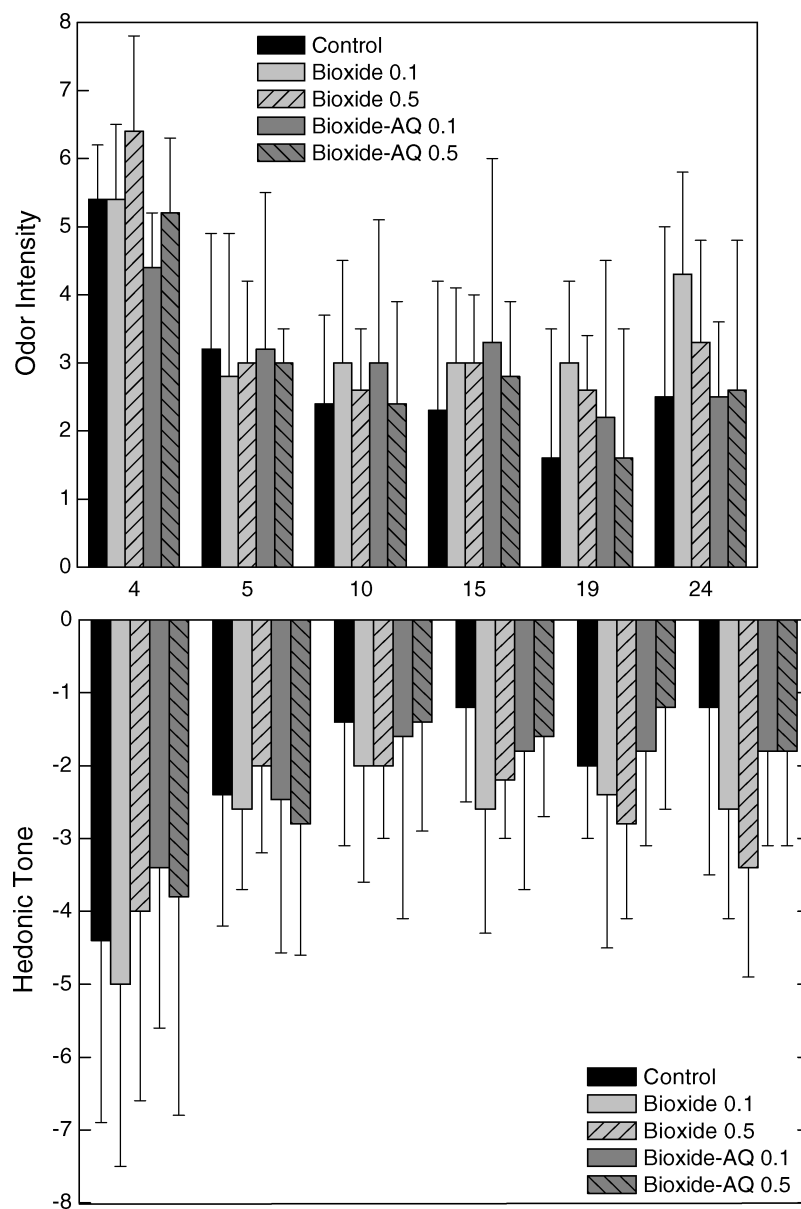


Figure 3: Odor intensity and hedonic tone of each sample over the period of study.

accumulated in the headspace of the buckets while they were closed. After the first test, a hole was made in the lid of each bucket, avoiding accumulation of odorants in the headspace. The odor intensity of all treatments appeared to remain unchanged throughout the experiment, indicating strong persistence of odors from the biosolids. Although the hedonic tone of samples treated with

Bioxide appears to be slightly worse than the control (Fig. 3(b)), the difference can be ignored considering the error levels associated with the study.

In terms of odor character, they described odors from the samples as “rotten fishy” or “ammoniacal” for all treatments, indicating that amines may have contributed to the odor character of the materials. As described above, the instrumental analysis showed levels above human detection thresholds for TMA in the headspace over the samples. The TMA results suggest that the odor panelist may have been heavily influenced by the presence of TMA. Ammonia was also likely present in the headspace due to the high pH caused by lime addition, although it was not measured, and may have contributed to the intensity of the odor. Nonetheless, considering its high odor threshold (around 5 ppm^[24]) and low persistency, the odorant causing the fishy or ammoniacal odor was probably TMA. Furthermore, the odor of TMA could mask that of other compounds, e.g., sulfur compounds, considering its contribution to the overall odor index of the samples. Twenty-four days after the treatment, the odor index of the sample with Bioxide 0.5 gal/ton of wet biosolids from TMA is 570 (odor index = concentration/odor threshold). That from MSH is 10.

In summary, although the instrumental analysis clearly showed the benefit of adding Bioxide to biosolids with respect to sulfur compound reduction, the effects on sensory odor detection could not be identified with the simple odor evaluation study. A more sophisticated sensory panel was required to properly evaluate odor control effectiveness of Bioxide.

CONCLUSIONS

A preliminary study on the odor control effect of addition of Bioxide or Bioxide-AQ to dewatered sludge during the liming process has been evaluated. The odors from the final products were evaluated with a simple odor evaluation panel and gas chromatography-mass spectrometry.

Through the simple odor evaluation study, the benefit of Bioxide addition to the biosolids could not be clearly observed, since all the evaluators reported similar level of fishy or ammoniacal smell from every sample. They could not identify other odors from the samples, e.g., odors from reduced sulfurs.

With results from the GC analysis of gases from the headspace of each sample, odor that the evaluators complained about could be related with TMA. Odor of TMA is typically characterized as fishy smell and is persistent over time. Therefore, it was hypothesized that odor caused by TMA masked all the other odors causing by sulfur compounds and dominated the overall odor character from each sample.

The hypothesis of TMA dominance in odors from biosolids was further supported with the time profiles of TRS and MSH. The samples with Bioxide or Bioxide-AQ produced up to 5 times lower TRS than the control. Therefore,

Bioxide, especially Bioxide-AQ, was very effective in reducing the production of the reduced sulfur compounds from biosolids.

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